STUDY ON MECHANICAL AND BARRIER PROPERTIES OF POLYURETHENAE-BASED NANOCOMPOSITE AS HIGH PERFORMANCE THERMAL BUILDING NANO INSULATION MATERIALS (NIMs)

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ABSTRACT

Polyurethanes (PUs) are unique polymer materials with a wide range of physical and chemical properties. With well-designed combinations of monomeric materials, PUs can be tailored to meet diversified demands of various applications such as coatings, adhesives, fibers, thermoplastic elastomers, and foams. However, PUs also have some disadvantages, such as low thermal stability and low mechanical strength, etc. To overcome these disadvantages, a great deal of effort has been devoted to the development of nanostructured polyurethane (PU)/montmorillonite (MMT) composites in recent years.

In general, the structures of polymer/clay nanocomposites are classified according to the level of intercalation and exfoliation of polymer chains into the clay galleries. Various parameters including clay nature, organic modifier, polymer matrix and preparation method are effective on the intercalation and exfoliation level. Therefore depending on the nature and properties of clay and polymer as well as preparation methodology of nanocomposite, different composite micro-structures can be obtained. The development of one a type of nanocomposites that is able to withstand high tensile strength and high barrier properties are the results to look for.

ABSTRAK

Poliuretana (PU) adalah bahan polimer yang unik dengan pelbagai ciri-ciri fizikal dan kimia. Dengan kombinasi yang direka dengan bahan-bahan monomeric, PU boleh disesuaikan untuk memenuhi permintaan pelbagai aplikasi seperti salutan, pelekat, serat, elastomer termoplastik dan buih. Walau bagaimanapun, PU juga mempunyai beberapa kelemahan, seperti kestabilan haba yang rendah, kekuatan mekanikal yang rendah dan lain-lain. Untuk mengatasi kelemahan ini, banyak usaha telah ditumpukan kepada pembangunan poliuretana bernanostruktur (PU) / montmorilonit (MMT) komposit sejak kebelakangan ini.

Pada umumnya, struktur-struktur nanokomposit polimer / tanah liat adalah dikelaskan mengikut tahap interkalasi dan pengelupasan rantai polimer ke dalam galeri tanah liat. Pelbagai parameter termasuk sifat tanah liat, pengubahsuai organik, matriks polimer dan kaedah penyediaan telah menjadi salah satu cara yang efektif pada interkalasi dan tahap pengelupasan. Oleh itu, komposit mikro-stuktur yang berbeza dapat diperolehi bergantung pada jenis dan sifat-sifat tanah liat dan polimer serta kaedah penyediaan nanocomposite. Pembangunan sejenis nanokomposit yang mampu menahan kekuatan tegangan yang tinggi dan ciri-ciri halangan yang tinggi adalah hasil untuk mencari.

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CHAPTER ONE

INTRODUCTION

1.1 Research Background

The construction and operation of buildings is responsible for significant environmental impacts, predominately through resource consumption, waste production and greenhouse gas emissions. Building insulation will be one of the main focuses, where the demand for more energy efficient buildings is expected to grow significantly in coming years. One of the main problems related to energy consumption in buildings is created by winter heating and summer cooling. The presence of glass surfaces and the insulating capacity of the outer cladding are the main reasons for heat loss and gain within the building envelope (Scalisi, 2009). Insulation is the most effective way to improve the energy efficiency of a home. Insulation of the building envelope helps keep heat in during the winter and keep solar heat away during summer to improve thermal comfort while saving energy. Insulation materials which are used for building insulation include mineral wool, cellulose batting, foam plastics and newly emerged materials like nanomaterial.

Forms of insulation are felt or plastic sheeting, sometimes with a reflective surface, installed directly below the tiles or other material; synthetic foam batting laid above the ceiling and recycled paper products and other such materials that can be inserted or sprayed into roof cavities. So called cool roofs are becoming increasingly popular, and in some cases are mandated by local codes. Cool roofs are defined as roofs with both high reflectivity and high thermal emittance. (Jelle et. al., 2010)

Malaysia, having a warm and dense climate makes roof insulation important. Poorly insulated and ventilated roofing can suffer from problems such as spaces below the roof absorb heat easily hence causing temperature to rise. These problems normally result in the installation of air-conditions which is uneconomical and bring damage to the environment.

A common material that is being used as paint application is plastic which is polymer by classification. Polymer is a high molecular weight compound that made up of multiple repeating structural units usually by covalent chemical bonds. The process polymerization is an action taking place where all monomers are linked together to form a polymer. Monomer is a group that can only consists of one or more substituted chemical groups. Polymer can be categorized into two classes – natural and synthetic. Natural polymers consists of examples like starch, cotton, proteins and wool while synthetic polymers has a wider range of properties.

Polymer alone is not enough as its properties consists of advantages and disadvantages. Material combinations and ranges have been, and are yet being, extended by the development of composite materials. A composite is considered to be any multiphase material that exhibits a significant proportion of the properties of both constituent phases such that a better combination of properties is realised. According to the principle of combined properties, better property combinations are fashioned by judicious combination of two or more distinct materials (Callister & Rethwisch, 2008).

A type of combination will be with nanotechnology. Nanotechnology is widely being used in the built environment for its advantages in many improved engineering properties of the nano materials. Nano insulating materials open up new possibilities for ecologically oriented sustainable infrastructure development. The most widely used nano material in built environment is for the purpose of insulation to improve the energy efficiency namely in the buildings and dwellings. Nanotechnology has now provided an effective and affordable means to increase energy efficiency in pre-existing buildings as well as new construction by increasing thermal resistance. The major advantage of nano insulation materials is its benefit of translucent coatings which increase the thermal envelope of a building without reducing the square footage. The intrinsic property of nano insulating material is it can be applied to windows to reduce heat transfer from solar radiation due it its thermal resistant property and the translucent property allows diffusing of day light. The nano insulating material has significant advantage in reducing the operational energy aspects of buildings due to its valuable insulating properties. (Gammampila et. al., 2010)

More than ten years before, nanocomposite based nano-layered silicates have attracted much attention due to its low cost, the availability and non-isometric structure that derived from a high aspect ratio of nanofillers. Even though the nanocomposite technology is

growing quickly, there are certain industries that still using the conventional composite or microcomposites. Previous research that conducted by Stec and Hull (2010) has proved that nano-layered silicates in the polymer matrix significantly increase strength and heat resistance although decrease in gas permeability and flammability is observed. However, a good dispersion of the organoclay in the polymer matrixes is crucial to achieve the improvement manner of polymer nanocomposite (Johanne *et. al.*, 2005). The intimate enclosure of nanoparticles in the polymer matrixes can change lots of the materials properties. The nanoparticles can serve as matrix reinforcement as transformation of material properties such as mechanical, chemical and morphological can as well be achieved. Nowadays, there are many researches based on the development of the polymer nanocomposite (Ujhelyioova, 2007).

Polymer nanocomposite benefited from improved barrier properties. The impact of nanofillers with high aspect ratio characteristic is trusted to increase this property by producing tortuous path, so that the gas molecules movement would be slow down passing through the nanocomposite matrix. Currently, there are many developments and publications on preparing polyurethane nanocomposite were established. Nevertheless, the study of polyurethane nanocomposite in the mechanism of development of polyurethane properties and the effect of nanofillers on the surface mechanical properties of polyurethane nanocomposite has received less attention. It is required to know the effect of nanofillers on the viscoelastic performance of polyurethane (Yusoh, 2010). Therefore the continuity of polymer nanocomposite study should be done to achieve better result in improving the characteristic.

1.2 Problem Statement

Nowadays, the traditional method commonly used to increase the thermal conductivity values is, by increasing the thicknesses of the insulation materials in the building envelopes. Nevertheless, the method is not applicable due to several reasons, considering space issues with respect to economy architectural restrictions and other limitations, material usage and existing building techniques. In the other hand, the recent studies pointed out that energy efficiency measures are the most cost-effective ones, whereas measures like solar photovoltaic and wind energy are far less cost-effective than insulation retrofit for buildings (Jelle, 2011).

Currently, polyurethane is more widely used as thermal insulation material rather than the other material such as expanded polystyrene (EPS) and extruded polystyrene (XPS). It is important to consider several factors on why polyurethane as a good thermal insulation material for the end used for coatings and the operating cost is selected. Firstly, the properties of modified polyurethane should be determined. The properties are hardness, strength, stiffness, permeability and expansion coefficient. Then, the barrier, mechanical and chemical behaviour of the modified polyurethane must be tested to examine the product is in the best quality and environmentally safe. Other than that, the thermal stress ought to minimize and provide good modified polyurethane adhesion (Chattopadhyay *et. al.*, 2006).

1.3 Objectives

1.3.1 To produce polyurethane-clay nanocomposites that is very thin yet has a high flame retardancy and resistance.

1.3.2 To study the barrier, mechanical and physical properties including permeability and resistance of polyurethane-clay nanocomposites.

1.4 Scope of Study

1.4.1 To fabricate very thin thermal building insulation materials (TIMs) using polyurethane-clay nanocomposites

1.4.2 To characterize the pristine polyurethane and polyurethane based nano-insulation-materials (NIMs) using field emission scanning electron microscopy (FESEM), gas absorption test, X-ray diffraction (XRD) and Fourier transform infrared spectrometer (FTIR)

1.4.3 To determine the permeability and permeability coefficient of the materials using a new fabricated gas permeability test. The purpose is to examine the permeability of the materials against presence of high pressure as well as the safety of PU-NIMs as thermal building insulation materials. Then, the samples will be tested for mechanical properties using tensile test.

1.5 Motivation

Currently, polyurethane has been widely used in industry as building materials regarding to its unique and versatile polymeric material. It is apply as thermal insulation materials, coatings, adhesives, foams and composites (Chen *et. al.*, 2000). These types of materials have received extraordinary attention for their synthesis, morphological, chemical and mechanical behaviour (Cai *et. al.,* 2009). However, PUs also has some disadvantages, such as high permeation rate and low mechanical strength, etc. In order to decrease the global warming effect, thermal efficiency building construction materials has been introduced to improve the energy efficiency of buildings. With the aim of achieving the demands of enhancing the energy efficiency of building by reducing the pore size of the nanocomposites, the thermal insulations of buildings play a crucial role. Therefore, new thermal insulation materials and solutions with low thermal conductivity values have been and are being pursued instead of improving the traditionally method which is increase thicknesses in the building coatings. Energy efficiency of buildings could be saved if they are properly designed and operated. In addition, a least cost energy strategy should be support by conservation of energy future. Therefore, resources of the energy will be saved by every unit of energy saved give measure of technology. Thus, the operating costs associated with energy unit generated will be reduced / eliminated. So, appropriate early design can be made on the subject of choosing the building components (Al-Homoud, 1997). Nevertheless, the thermal insulation materials will support the world-wide campaign in order to reduce the heat reaches on our earth. One promising method for reducing the energy consumption of building systems is by introducing the thermal nano insulation materials (NIMs) either as outer layers or by sandwiched inner layers using polyurethane nanocomposites. Thus in this research work the potential application of polyurethane nanocomposites as a thermal insulation building materials has been developed as an alternative solution to conventional insulation materials such as extruded polystyrene and the experimental work are carried out to examine the thermal conductivity and the effect of nano-pore of PU nanocomposites to the final properties of polyurethane nano insulation materials (PU-NIMs). Besides that, a series of thermal conductivity assessment (TCA) is conducted and the experimental data from thermal conductivity are validated through the modified TCA models to predict the PU-NIMs surface temperature. Major expected outcome in this work is to achieve the highest possible thermal insulation resistance using new synthesis insulation materials as a solution for improving the energy efficiency for building material applications.

CHAPTER TWO

LITERATURE REVIEW

2.1 Polyurethane

Polyurethane is a polymer composed of a chain of organic units joined by carbamate (urethane) links. While most polyurethanes are thermosetting polymers that do not melt when heated, thermoplastic polyurethanes are also available.

Polyurethane polymers are formed by reacting an isocyanate with a polyol. Both the isocyanates and polyols used to make polyurethanes contain on average two or more functional groups per molecule. Polyurethane products often are simply called "urethanes", but should not be confused with ethyl carbamate, which is also called urethane. Polyurethanes neither contain nor are produced from ethyl carbamate (Chen, et al., 2012).

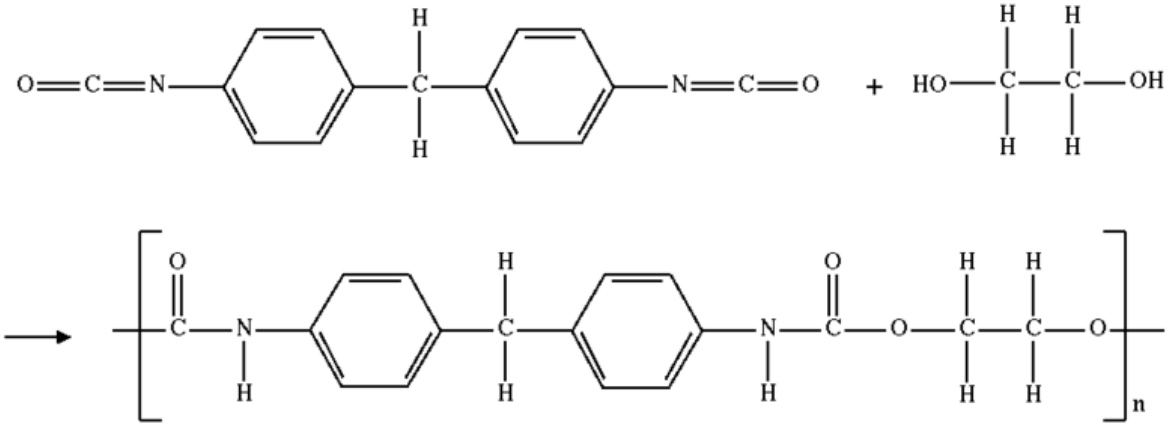

Figure 2.1: Formation of polyurethane from isocynates with polylol. (Olad, 2011)

Polyurethanes are one of the most versatile materials in the world today. Their many uses range from flexible foam in upholstered furniture, to rigid foam as insulation in walls, roofs and appliances to thermoplastic polyurethane used in medical devices and footwear, to coatings, adhesives, sealants and elastomers used on floors and automotive interiors. Polyurethanes have increasingly been used during the past thirty years in a variety of applications due to their comfort, cost benefits, energy savings and potential environmental soundness (Khalid et. al., 2007).

Polyurethane durability contributes significantly to the long lifetimes of many products. The extensions of product life cycle and resource conservation are important environmental considerations that often favor the selection of polyurethanes. Polyurethanes (PUs) represent an important class of thermoplastic and thermoset polymers as their mechanical, thermal, and chemical properties can be tailored by the reaction of various polyols and polyisocyanates.

Polyurethanes (PUs) are unique polymer materials with a wide range of physical and chemical properties. With well-designed combinations of monomeric materials, PUs can be tailored to meet diversified demands of various applications such as coatings, adhesives, fibers, thermoplastic elastomers, and foams. However, PUs also have some disadvantages, such as low thermal stability and low mechanical strength, etc. To overcome these disadvantages, a great deal of effort has been devoted to the development of nanostructured polyurethane (PU)/montmorillonite (MMT) composites in recent years (Cao, et al., 2004).

2.2 Polymer-clay Nanocomposite

Nanocomposites are polymers containing nanofillers (Pinnavaia & Beall, 2000). The microstructure of nanocomposites has inhomogeneities in the scale range of nanometers. Nanocomposite materials cover the range between inorganic glasses and organic polymers (Paul & Robeson, 2008). Fillers of polymers have been used for a long time with the goal of enhanced performance of polymers, and especially of rubber. Polymer–clay nanocomposites were reported in the literature as early as 1961 (Novak, 1993). Nanocomposites demonstrate often unusual and beneficial for the user properties. Scientific and technical literature report the improvement or enhancement of properties of polymer nanocomposites compared to the pristine polymers. This vague statement means an improvement of polymer properties from the standpoint of polymer application.

The main paradigm is that a valuable nanocomposite is one with the largest possible surface of nanofiller. In practice it means avoiding aggregation of nanoparticles and exfoliation of nanoclays. Nanoparticles are commercially available from different sources. Sols of nanosilica as colloid solutions in water or in organic solvents are used in preparation of PU nanocomposites. Fumed silica is available as individual particles ranging from 10–20 nm to micrometers, and can be more or less successfully dispersed in a polymer (Blumstein, 1961).

Layered alumosilicates clays and especially montmorillonite (bentonite) are widely used in nanocomposites. Silicates have a characteristic distance between galleries of 1 nm; the basal spacing of a gallery is also ca. 1 nm. Inorganic cations like Na+ between galleries hold negatively charged galleries together. The replacement of the inorganic cations in the galleries of the native clay by alkylammonium (onium) salts or quarternary amines with long alkyl substituents (surfactants) leads to a better compatibility between the inorganic clay and hydrophobic polymer matrix. The replacement leads to an increase of the space between galleries facilitating intercalation of polymer molecules into the clay. Unless stated otherwise, in this paper we will describe only such onium salt modified montmorillonites. This is later define as organoclay. Three main types of nanocomposites are schematically presented in Figure 2.3.

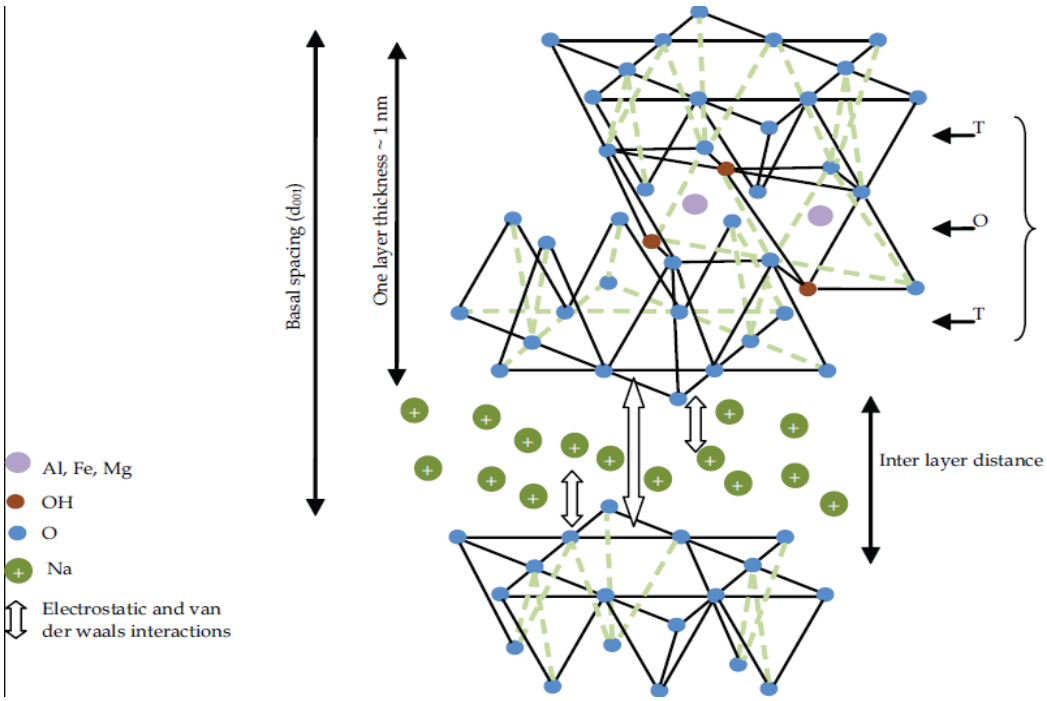

Figure 2.2: A sample of organoclay structure (montmorillonite) (Olad, 2011)

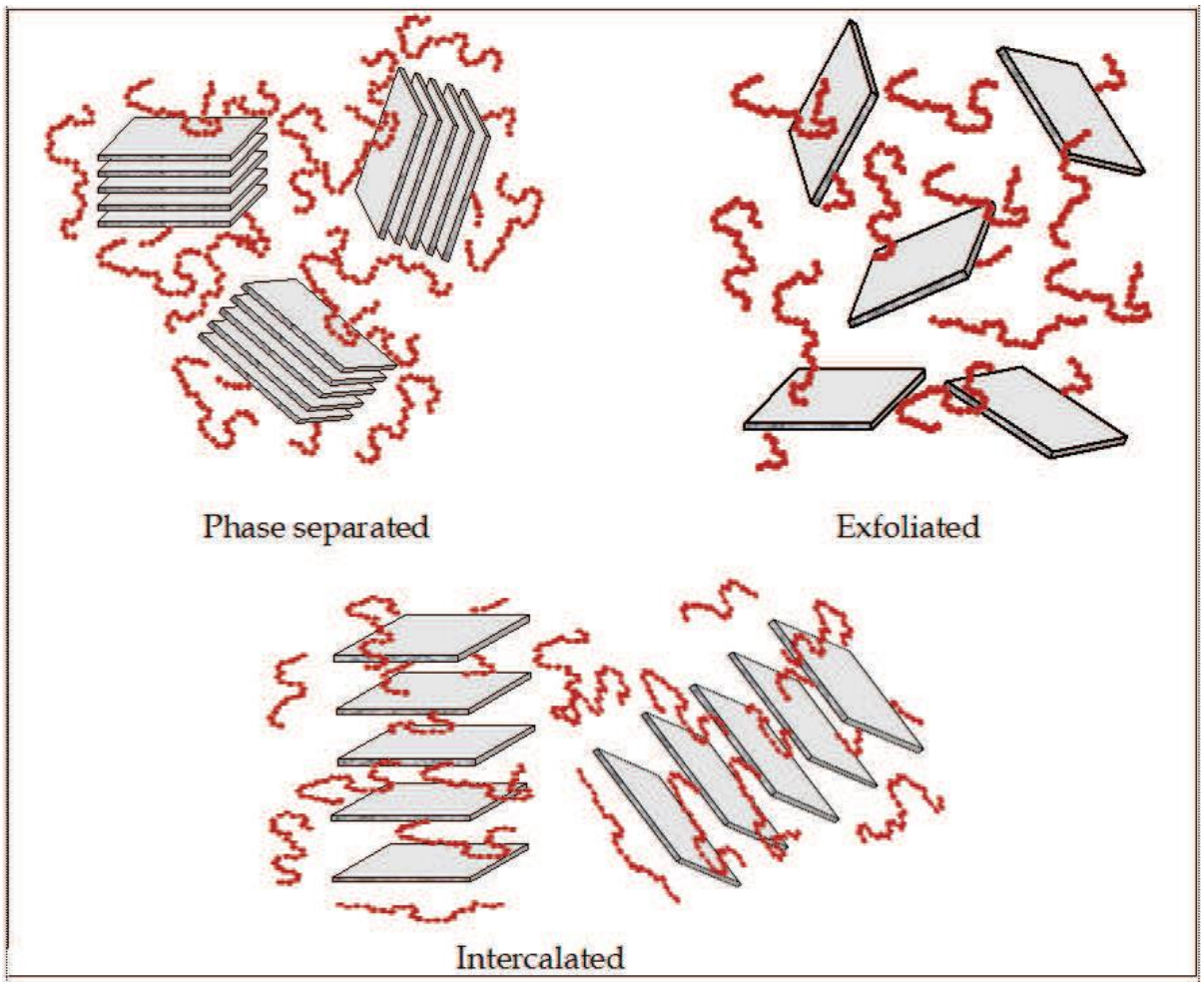

Figure 2.3: Types of nanocomposite structure (Olad, 2011)

In most cases exfoliated nanocomposites with a high aspect ratio demonstrate enhanced properties compared to the same pristine polymers or polymer with smectic clay. Usually the exfoliation of clay nanolayers in a polymer matrix requires polarity match between the clay surface and the prepolymer precursors to allow optimal access to the gallery (Triantafillidis, LeBaron, & Pinnavaia, 2002). The morphology of nanocomposites is usually studied by X-ray techniques (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Sanyal, Datta, & Hazra, 2002).

2.3 Nanocomposite structure

In general, the structures of polymer/clay nanocomposites are classified according to the level of intercalation and exfoliation of polymer chains into the clay galleries. Various parameters including clay nature, organic modifier, polymer matrix and preparation method are affective on the intercalation and exfoliation level. Therefore depending on the nature and

properties of clay and polymer as well as preparation methodology of nanocomposite, different composite micro-structures can be obtained.

2.3.1 Phase separated structure

Phase separated structure is obtained when the organic polymer is interacted with inorganic clay (unmodified clay), the polymer is unable to intercalate within the clay layers and the clay is dispersed as aggregates or particles with layers stacked together within the polymer matrix. The obtained composite structure is considered as "phase separated". The properties of phase separated polymer/clay composites are in the range of traditional micro composites.

2.3.2 Intercalated structure

Intercalated structure happens when one or more polymer chains are inserted into the inter layer space and cause to the increasing of the inter layer spacing, but the periodic array of the clay layer is still exist, the intercalated nanocomposite is formed. The presence of polymer chains in the galleries causes to the decreasing of electrostatic forces between the layers but it is not totally dissolved. A well-ordered multilayer hybrid morphology with a high interference interactions consisted of polymer chains and clay layer is obtained in this configuration.

2.3.3 Exfoliated structure

Exfoliated or delaminated structure is obtained when the insertion of polymer chains into the clay galleries causes to the separation of the layers one another and individual layers are dispersed within the polymer matrix. At all, when the polymer chains cause to the increasing of interlayer spacing more than 80-100 Å, the exfoliated structure is obtained. Due to the well dispersion of individual clay layers, high aspect ratio is obtained and lower clay content is needed for exfoliated nanocomposites. Also most significant improvement in polymer properties is obtained due to the large surface interactions between polymer and clay. Various polymer/clay structural configurations.

2.4 Preparation of polymer/clay nanocomposites

Many efforts have been made for the preparation of intercalated and exfoliated polymer/clay nanocomposites with improved properties. A variety of polymer characteristics including polarity, molecular weight, hydrophobicity, reactive groups as well as clay characteristics such as charge density and its modified structure and polarity are affective on the intercalation of polymer chains within the clay galleries. Therefore different synthetic approaches have been used for the preparation of polymer/clay nanocomposites. In general there are four preparation methods including insitu template synthesis, solution intercalation, insitu intercalative polymerization and melt intercalation.

2.4.1 Sol gel synthesis

In this method the clay layers are synthesized in situ in the presence of polymer chains. The polymer and clay primary materials are dissolved in an aqueous solution. Typically magnesium hydroxide, silica and lithium fluoride as clay building blocks are mixed with polymer in a solvent. The gel or slurry is refluxed usually at high temperatures followed by washing and drying. The nucleation and growth of clay layers are take place on the polymer chains and the polymer chains are trapped in the clay inter layers. Although the clay layers may be well dispersed within the polymer matrix without the modification of clay by onium cations, however this method has serious disadvantages. The high temperature applied for the synthesis of clay layers causes to the decomposition of polymers. Only hectorite clay is synthesized at the lower temperatures. Also the synthesized clay crystals, generated by the self-assembly process, have tendency to aggregate. Therefore this method is not widely used and only a few nanocomposites using hectorite clay and poly (vinyl alcohol), polyaniline and polyacrylonitrile have been synthesized by this method (Alexendre & Dubois, 2000).

2.4.2 Solution intercalation

In this method the polymer or prepolymer is dissolved in a solvent and the clay is dispersed in the same solution. The clay is swollen in the solvent and the polymer chains intercalate between the layers. The intercalated nanocomposite is obtained by solvent removal through vaporization or precipitation. Clays can be swollen easily in solvents such as water, acetone, chloroform and toluene. Delaminated sheets are then used for the absorption of the polymer chains. The entropy gained during the solvent evaporation by the exit of solvent molecules from the interlayer spacing, allows the polymer chains to diffuse between

the layers. We have used the solution intercalation method for the preparation of epoxy /clay nanocomposites. Diglycidyl ether bisphenol A (DGEBA), (196-208 epoxy equivalent weight, Epiran–05, Khouzestan Petrochemical Company, Iran), was used as the polymer matrix. EPIKURE curing agent 3200, Aminoethylpiperazine (AEP) from Hexion Specialty Chemicals Inc., was used both as curing agent of epoxy resin and also as intercalating agent for montmorillonite (MMT). The inorganic clay used in this study was K-10 grade MMT obtained from Sigma-Aldrich Co (USA) with a surface area of 130 m2/g. Organically modified clays, Cloisite 30B (d-spacing = 18.5 Å) and Cloisite 15A (d-spacing = 29.88 Å) were provided by the Southern Clay Products. Tetraethylammonium chloride (TEA) salt was also used as intercalating agent of MMT. Acetone was used as solvent. Depending on the interactions between polymer and clay sheets, intercalated or exfoliated structures may be obtained in this method. This technique is used for the preparation of epoxy/clay nanocomposites. However due to the need for use solvent, this technique cannot be applied in industry. The nanocomposite preparation by emulsion polymerization, with the clays dispersed in the aqueous solution, is also categorized as solvent intercalation method (Rehab & Salahuddin, 2005). Toyota group has been used this technique to produce polyimide/clay nanocomposites (Yano et al., 1993). The emulsion and bulk polymerization methods have been used for the preparation of polystyrene/clay nanocomposites using the Na-MMT, cloisite 30B and cloisite 15A clay materials. The effect of clay swelling method and sonication on the inter layer spacing and intercalation have been investigated. Good dispersion of Na-MMT in the polystyrene (PS) matrix was observed when an emulsion polymerization was employed and good dispersion of cloisite 30B in the PS was observed during bulk polymerization. Cloisite 30B showed better dispersion when this clay was swollen with the monomer during emulsion polymerization. Sonication had good effect on dispersion of the clays in the PS matrix. PS/Cloisite 15A nanocomposites showed minor increase in d-spacing compared to the pure cloisite 15A. TGA analysis showed that the thermal stability of the nanocomposites has been improved compared to the pure polystyrene.

2.4.3 Insitu intercalative polymerization

This technique was the first method used for the preparation of polymer/clay nanocomposite by Toyota research group in the preparation of Nylon-6 nanocomposite from caprolactam monomer (Usuki et al., 1993). In this method the organoclay is swollen in monomer liquid or monomer solution. The monomers diffused into the inter layer spacing are

polymerized by the heat or radiation, by the diffusion of an initiator or by the organic initiator present on the organic modifier of clay (Hussain et al., 2006). The polymerization is carried out within the clay galleries as well as extra galleries. The growth of polymer chains results to the exfoliation and formation of disordered structure.

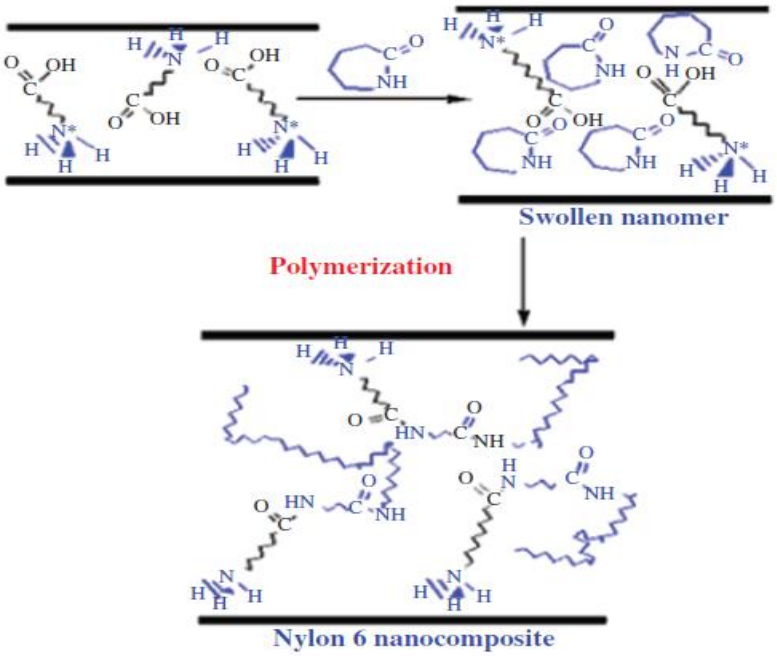

Figure 2.4: Formation of Nylon-6 nanocomposite through in situ polymerization with ADA-MMT (http://nanocor.com)

This method is suitable for the preparation of thermoset/clay nanocomposites and has been widely used for the epoxies and styrenic polymer nanocomposites (Lan, Kaviratna, & Pinnavaia, 1995). The polarity of monomer and clay layers determines the diffusion rate and equilibrium concentration of monomer within the clay galleries. Consequently the exfoliation and dispersion of clay layers can be tailored by the clay and monomer chemistry (Paviladou & Papaspyrides, 2008). Polyaniline/MMT nanocomposites have been prepared by the insitu polymerization of aniline in the presence of MMT (Olad & Rashidzadeh, 293-298). Both unmodified and organomodified MMT were used in the preparation of nanocomposites. Due to the using of acidic aqueous solutions for the polymerization of aniline, the polar organic anilinium cations can be interact with both unmodified and modified clays.

2.4.4 Melt intercalation

Clay is mixed within the polymer matrix in molten temperature. The conventional methods such as extrusion and injection molding are used for dispersion of clay layers within the polymer matrix. This method is effective technique for the preparation of thermoplastic nanocomposites (Kornmann, Linderberg, & Bergund, 2001). The polymer chains are intercalated or exfoliated into the galleries. Clays are organically modified and polymer chains are surface modified with more polar functional groups to enhance their compatibility and therefore promote the exfoliation. In melt intercalation method no solvent is required and it has many advantages for the preparation of nanocomposites and is a popular method for industry (Ray et al., 2003).

2.5 Previous work on PU-Organoclay Composites

A very impressive industrial application of nanocomposites was demonstrated by the Toyota Group in 1988 (Usuki et al., 1993). By using organoclay, they were able to polymerize ε-caprolactam in the interlayer gallery region of clay to form Nylon 6-clay hybrid. At a loading of only 4.2 wt% the tensile modulus doubled, the tensile strength increased more than 50%, and heat distortion temperature (HDT) increased by 80◦ C compared to the pristine polymer. The key to this extraordinary performance of Nylon 6-clay nanocomposites was explained as the complete exfoliation of the clay nanolayers in the polymer matrix (Usuki et al., 1993). This remarkable result stimulated many chemists to search for dramatic improvement of polymer properties upon addition of low level of organoclay.

The effects of organoclays on the properties of PU were studied (Pinnavaia & Beall, 2000), PU were prepared by the following procedures: (i) distribution of clay in polyol with a subsequent reaction with diisocyanate; (ii) interaction of PU with clay in organic solvent with a subsequent evaporation of solvent; (iii) reaction of diisocyanate with hydroxyalkyl groups of organic modifier in the clay with a subsequent reaction with polyol.

PU nanocomposites prepared with 1–6 wt% of clay demonstrate peaks on XRD patterns with a distance between galleries (basal spacing) in the range of 1.6–3.2 nm depending on the clay nature and its level (Chang & An, 2002). It is possible to conclude based on XRD and SEM and other spectroscopy, that polymer intercalated into the organoclay, it is not exfoliated, and organoclay is not homogeneously dispersed in a PU matrix. Many composites with an added non-exfoliated clay still demonstrate improved

mechanical and physical properties and thermal stability, lower permeability of dioxygen compared to the pristine PU. At the same time presented data of property vs organoclay level are not simple in a series of similar nanocomposites: it can be a curve with a maximum (minimum), it can be a permanent decrease or an increase of a property. It is documented that high temperature resistance of PU nanaocomposites is higher than that of pristine PU (Chang & An, 2002).

Wang and Pinnavaia prepared PU nanocomposites by solvation of organoclay by polyol first. Loading of polyol with clay up to 10–20 wt% makes a pourable mixture. XRD demonstrates that intercalation of polyol into clay results in an increase of with basal spacing from 1.8–2.3 nm to 3.2–3.9 nm. Such spacing testifies that there is intercalation of polyol into clay. Formation of PU results in further increase of basal spacing up to more than 5 nm. The latter case may be considered as exfoliation of a clay or dispersal of nanolayers. Important, that onium ions of the clay were considered as active reagents for coupling with diisocyanate. Loading of PU with 5–10 wt% of clay results in a two-three times improvement of tensile properties of a polymer, namely increase of strain-at-break, tensile modulus and tensile strength (Wang & Pinnavaia, 1998).

Common inorganic fillers are commonly used in PU chemistry to reduce formation cost and to increase stiffness, but the improvements in modulus for conventional PU composites are compromised by a sacrifice of elastomer properties.

The nanocomposites reported according to Wang and Pinnavaia, 1998 exhibited an improvement in both elasticity and tensile modulus. Clay nanolayers, even when aggregated in the form of intercalated tactoids, strengthen, stiffen and toughen the matrix in the studied case.

The enhancement in strength and modulus is directly attributed to the reinforcement provided by the disperse clay nanolayers. The improvement in elasticity is tentatively attributed to the plasticizing effect of onium ions, which contribute to dangling chain formation in the matrix, as well as to conformational effects on the polymer at the clay–matrix interface.

A complete exfoliation of nanoclay was observed in PU nanocomposites with high concentration of nanoclay (up to 40%) (Ni, et al., 2006). In this work organoclay was additionally functionalized with diamine, which served a chain extender under PU

nanocomposite formation. Tensile strength and elongation-to-break reaches maximum at 5 wt% of nanofiller loading (Ni, et al., 2006). Another study of PU nanocomposites demonstrates that the maximum values of flexural and tensile strengths are obtained at only few percent of a clay content (Seo, et al., 2006) Several PU nanocomposites prepared in (Chang & An, 2002) were studied in the range of organoclay loading of 0–8 wt%. Tensile properties demonstrate optimal properties at 3–4 wt% loading by different organoclays. Ultimate strength and initial modulus have increased in nanocomposites, as well as increased gas barrier properties, the thermal stability of one nanocomposite only increased with increasing clay content (Chang & An, 2002). A gradual increase of tensile strength with clay content increase up to 5 wt% of PU nanocomposites and only slight increase of glass-transition temperature (Tg) and slight increase of thermal stability was observed for PU nanocomposites prepared in Ref. (Pattanayak & Jana, 2005). It was concluded based on WAXD and TEM that PU intercalated into clay galleries (Pattanayak & Jana, 2005).

Organically-treated synthetic fluoromica, which is a layered silicate as well, of different size has a modest effect on the properties of PU nanocomposites (Paul & Robeson, Polymer nanotechnology: Nanocomposites, 2008). Exfoliated in a solvent unmodified clay laponite as a hydrophilic compound interacts with polar soft segments (polyol) in PU like poly(ethylene oxide) or poly(propylene oxide) whereas in PU with hydrophobic soft segments like poly(tetramethylene oxide) clay interacts with the hard domain (urethane links) (Finnigan, et al., 2006). Thus, in the first case a decrease toughness and elongation-to-break is observed, whereas in the second case an increase of the same properties is observed (Finnigan, et al., 2006). Such a study gives a better understanding of the nanoclay effect of PU nanocomposites properties.

It is reasonable to expect that the formation of PU nanocomposites leads not only to improvement of all valuable for the user properties of the pristine PU. The PU nanocomposites studied in Jin, et al. (2006), journal demonstrated an increase in the elasticity, decrease in damping property, significant increase in thermal stability but demonstrated also a decrease of tensile modulus. Hysteresis results indicate that energy dissipation increases with an organoclay concentration increase (Jin, Song, Yao, & Chen, 2006). Films of radiation-curable urethane acrylates demonstrate minor variation of Young's modulus and tensile strength upon dispersion of organoclay in formulations in the concentration up to 5 wt% (Uhl, Davuluri, Wong, & Webster, 2004). Some onium salts of organoclay have ω-hydroxyalkyl

substituents. The HO– CH2– group can be used to react with isocyanate and, that way, to drag OCN–R between galleries or at least strengthen the interaction between urethane pre-polymer and clay (Pattanayak & Jana, 2005). A twofold increase of tensile strength and tensile modulus in exfoliated nanocomposites was obtained (Pattanayak & Jana, 2005). In a quite similar way PU nanocomposites are formed by a reaction of IPDI not only with polyol but with HO–CH2– groups within galleries. Probably nanocomposites have an intercalated structure (Solarski, et al., 2005).

PU nanocomposites with the photoinitiator (PI) 2-hydroxy-2-methyl-1-phenylpropane-1-one were prepared (Tan & Nie, 2007). This PI-PU nanocomposite was dispersed in polymerizable resins. Such initiator manifested high efficiency. XRD and TEM demonstrated formation of intercalated and exfoliated UV-cured nanocomposites with many good characteristics. Photopolymerization occurs inside the organoclay galleries (Tan & Nie, 2007).

PU, as well as a number of other polymers, can demonstrate shape recovery after temporary applied stress (shape memory). PU nanocomposites demonstrated the lowest relaxation rate after removal of a stress 1 wt% of organoclay. The studied PU nanocomposites manifested the highest degree of clay exfoliation namely at 1 wt%. PU nanocomposites with 3 and 5 wt% of organoclay relaxed faster than the pristine PU (Cao & Jana, 2007).

A profound improvement of properties PU foam upon addition of 5 wt% of organoclay was observed (Cao X. , Lee, Widya, & Macosko, 2005).

The use of organoclay Cloisite® 15A of Southern Clay Products as received. A distance between the galleries in the Closite is 3.15 nm (Zhu & Wool, 2006). Urethane acrylate oligomers were prepared the usual way: a reaction of polyol with diisocyanate with a subsequent capping of non-reacted isocyanate groups by ω-hydroxyalkyl acrylates. Prior to that Cloisite was dispersed in polyol by prolong high shear mixing. Unfortunately, this Cloisite and several other studied nanoclays of a similar structure efficiently catalyze di- and, especially trimerization of common isocyanates at elevated temperatures (Dodge, 2003)